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THERMAL ANALYSIS OF THE STABILITY OF POLYVINYLCHLORIDE

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ABSTRACT

DTA correlates well with the standard congo red test for the thermal stability of polyvinylchloride (PVC). Thermogravimetry is not sufficiently sensitive and the heat stability test is the least useful of all.

INTRODUCTION

Polyvinyl chloride (PVC) is one of the most widely used plastics. but it is unstable at evelated temperature. PVC degrades by an unzipping mechanism above 70°C, producing hydrogen chloride and normal processing temperatures are between 150°C and 200°C. The addition of compounding ingredients: impact modifiers, processing aids, pigments, fillers, lubricants, extenders, plasticisers and stabilisers, can radically effect the thermal stability of the material.

The inclusion of chloroparaffins into PVC significantly reduces the stability to heat and light of both stabilised and unstabilised compounds. The current work is part of an attempt to classify the stabilising effect in terms of the molecular structure of the organic additive.

The experimental techniques chosen to investigate the change in thermal stability were a modified congo red test (CRT), isothermal DTA, oven heat stability (OHS) and thermogravimetry.

EXPERIMENTAL

S67/113 is a medium mol.wt. suspension homo-polymer, Cereclor S45 (I.C.I.) is a chlorinated paraffin extender giving good low temperature properties in PVC.

The stabilisers used were:- mono ethanolamine (MEA); di ethanolamine (DEA); tri ethanolamine (TEA); mono-n-propanolamine (MPA); di-N-methyl aniline (DMA); hexamine (HEX); melamine (MEL); pentaerythritol (PENTA); tri-n-butylamine (TBA); diphenyl amine (DPA); triphenylamine (TPA); triphenylmethane (TPM); triphenylcarbinol (TPC); hexamethylmethylolmelamine (HMMM); trimethylolmelamine (TMM). The other ingredients were all laboratory standard materials.

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The formulations used were:-

	Formulation A	Formulation B
	parts	parts
PVC Corvic S67/113 (I.C.I.)	100	100
D.O.P.	50	25
Cereclor S45	-	25
Stabiliser	4.5	4.5
Antioxidant (Bisphenol A)	0.25	0.25

The sheets were prepared on a laboratory 2 roll mill, heated by steam to 155°C to 165°C.

The congo red test was based on B.S. 2782 Part 1 Method 130A (1976).

ISOTHERMAL DIFFERENTIAL THERMAL ANALYSIS

A DuPont 900 Differential Thermal Analyser was used isothermally at 200°C using the high temperature cell. Silica was used as the reference material. The sample was heated to 200°C at the maximum rate possible under an atmosphere of nitrogen at a flow rate 150 mls/minute. When all the stabiliser in the PVC had been consumed an exothermic peak was visible. The time taken from beginning the heat up to the peak of the exotherm was taken as a measure of the stability of the sample.

OVEN HEAT STABILITY TESTS

Samples were heated in a forced air convection oven at either 200 $\pm$ 1°C or 180 $\pm$ 1°C and removed at regular intervals. The colour changes were used to determine the relative stabilities of the samples.

RESULTS

The results are given in Table 1 for the isothermal data and congo red tests (CR). The correlation between the tests is very good. The value for students "t" test is 0.171 which is significant at the 10% level.

Thermogravimetry has been used to investigate the thermal degradation of pvc but in our experiments the sensitivity of TG was much lower than that of the DTA and so no further results were obtained.

In the early days of thermal analysis TG was claimed to be potentially more accurate than DTA; this claim was shown to be erroneous and current work confirms that calorimetric techniques are to be preferred to gravimetric methods.

The congo red test has the advantages of simplicity, cheapness and the ability to process a number of samples simultaneously, hence making it a useful tool in screening a large number of possible additives. Reproducibility of

results is good.

The oven stability test is commonly used in industry. The results could be misleading because of the use of colour changes to determine when degradation had taken place. It was difficult to differentiate between those that had given slightly different congo red times because an additive or stabiliser system which gives good colour hold is not necessarily the one that gives a long congo red time. The general trend of stabilities is similar for both the congo red test and oven stability test.

CONCLUSIONS

Isothermal DTA correlates well with the standard congo red test and could provide the basis for a more convenient quality control test. The smallness of the DTA sample however makes the obtaining of a homogeneous sample more difficult and this will militate against the adoption of DTA as a standard. Inhomogeneous specimens may also contribute to the poor reproducibility of thermogravimetry.

The colour change on heating has little to recommend it apart from simplicity and should be discontinued.

TABLE 1 Comparison of the congo red test and isothermal dta on the reduction in stability of PVC caused by the addition of S45.

Additive	Congo red test	
None	-61	-54
MEA	-46	-57
DEA	-39	-39
TEA	-35	-29
MPA	-39	-41
DMA	-56	-53
HEX	-11	-33
MEL	-34	-36
PENTA	-55	-55
TBA	-51	-57
DPA	-60	-62
TPA	-65	-61
TPM	-64	-64
TPC	-64	-53
HMMM	-37	-38
TMM	-37	-35